A comparative study of the dispersion of carbon nanofibres in polymer melts

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Abstract. The dispersion of carbon nanofibres (CNF) in a polymer matrix using two melt mixing methods is studied. Distributive and dispersive mixing were evaluated by optical and electron microscopy. The CNF were chemically modified to improve the interface with the matrix. The results showed that the two methods produced good distribution of the filler, but extensional stresses induced higher dispersion. The latter correlated well with a decrease in electrical resistivity. Also, the chemical modification largely improved the CNF/polymer interface.

Introduction

Polymer nanocomposites containing carbon nanofibers are being increasingly used in electromagnetic interference shielding and electrostatic discharge protection [1], sensors for organic vapors [2], electrostatic painting of exterior automotive panels and shielding of automotive electronics, among others. They can be prepared via in-situ polymerization, solution processing and melt mixing [3]. The last is the most attractive, as it is environmentally benign, simple and easily scalable to industrial production. Co-rotating twin screw extruders are often used, while at laboratory scale batch mixers and micro-compounders are also popular.

A major concern during the preparation of CNF/polymer nanocomposites is reaching sufficient dispersion levels, as these are associated to good mechanical properties. The effect of dispersion on electric properties is less consensual, as both a direct correlation between dispersion and electric conductivity [4] and the existence of an optimal dispersion level [5] have been reported. Therefore, it is not surprising that the dispersion of nanofillers in polymer matrices has been extensively studied in recent years [6,7]. For example, Lin *et al* [8] showed that the type of melt mixing equipment can affect *ab initio* the dispersion efficiency, since this depends on the flow fields generated. Extruders can generate high shear and create enough elongational stresses to break up the nanofiller agglomerates. However, composites prepared by the same method can exhibit different dispersion. For instance, Kasaliwal *et al* [9] showed that mixing speed and time in a microcompounder affect strongly the properties of polycarbonate/CNT composites. The nanofiller characteristics should also play a role in dispersion. Treating the CNF surface should decrease the high chemical inertia of pure CNF and improve dispersion in the matrix [10, 11].

In this work, carbon nanofibers were melt mixed with polypropylene using two mixing devices, namely a mini co-rotating twin-screw extruder and a device generating a series of converging-diverging flows, thus with a strong extensional flow component. The CNFs were used as-received, or functionalized. Distributive and dispersive mixing levels were assessed in all cases and correlated with electrical resistivity.

Experimental

Materials. The carbon nanofibers were produced by Applied Sciences Inc. (PR-24-PS grade). They are cylindrical and hollow, have a diameter ranging between 60 and 150 nm and the length can reach 100 μm. They are characterized by a graphitic layer structure with "stacked-cup" morphology [12]. These nanofillers form agglomerates with diameters up to several micrometers.

The polypropylene used was Stamylan P 13E10 from DSM (MFI= 0.5 g/10min, at 230 ºC/2.16 kg). A polypropylene grafted with maleic anhydride (PP-g-MA), Orvac CA100 from Arkema (MFI= 10

g/10min, at 190 ºC/0.325 kg), containing 1% of maleic anhydride, was used to react with the chemical groups introduced by functionalization of the CNF surface.

Chemical functionalization of the carbon nanofibers. The functionalization was based on the 1,3-dipolar cycloaddition reaction of azomethyne ylides [13] (see conditions in [11]). The functionalization was tailored to produce pyrrolidine groups at the CNF surface; it is expected to improve the CNF/matrix interface through the chemical reaction between the anhydride grafted on the PP and the cyclic amine groups at the CNF surface, forming amide links and covalently bonding PP molecules to its surface.

Composite preparation. PP and PP-g-MA pellets were ground into powder form in a Retzch grinder ZM 100, under liquid nitrogen. Polymer/CNF composites 95/5 w/w were prepared, either with as received or functionalized filler. Also, the polymer was either PP, or a PP/ PP-g-MA 80/20 w/w blend. The materials were pre-mixed, followed by melt mixing using three different methods:

i) “”TWIN” - using a co-rotating mini twin-screw extruder (see screw profile in Figure 1), with a flow rate of 270 g/h (set by a mini-feeder), screws rotating at 60 rpm, a flat temperature profile of 220 °C and a rod die;

ii) ”RINGS” - forcing the melt through a series of 12 stacked dies inducing a sequence of converging/diverging flows (8:1 compression ratio). The entire set-up was placed inside the reservoir of a capillary rheometer and could be disassembled to collect samples along the flow axis (Figure 1). After heating the material in the rheometer to 220 °C, the ram moved downwards at 6.25 mm/min;

iii) “TWIN+RINGS” - after preparing the composite in the extruder, the extrudate was cut into pellets and forced through the sequence of rings. Each step was performed under the conditions described above.

The composite obtained from each method was cut into pellets and compression moulded at 230 °C into 1 mm thick plates.

Characterization. The CNF were characterized by thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The samples were heated in a Q500 thermobalance from TA Instruments from 60 to 700 ºC at 5 °C/min under a constant flow of N2 (g). XPS spectra were obtained with a ESCALAB 200A-VG SCIENTIFIC spectrometer, using a Mg/Al double X-ray source with a power of 300W.

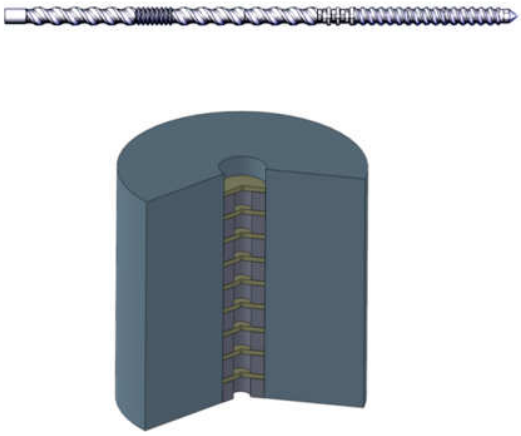


Fig. 1. Melt mixers used in this work: top - twin screw extruder; bottom - series of rings with alternating diameters in a capillary rheometer

The volume resistivity of the samples was obtained by measuring the characteristic I-V curves at room temperature with a Keithley 6487 picoammeter/ voltage source. The samples were previously coated by thermal evaporation with aluminium electrodes, where the probe tips touched the sample, and placed on the sample holder.

Optical microscopy (OM) using a BH2 Olympus transmission microscope was performed on 5 µm thick samples. An average area of $3{,}1 \times 10^5$ µm^2 was analyzed. The images acquired with a digital camera LEICA DFC 280 were characterized with the Leica Qwin Pro software in terms of the area ratio (A_r), representing the area of undispersed primary agglomerates:

$$A_r = \frac{A_{CNF}}{A_0} \times 100\% \qquad (1)$$

where A_{CNF} is the area covered by agglomerates and A_0 the total sample area.

Scanning electron microscopy (SEM) of cryo-fractured samples was performed on a LEICA-S360.

Results and Discussion

Although A_r is often used to assess the macrodispersion in nanocomposites [14,15], other indices could provide further useful information, such as the number of agglomerates per unit area, the average agglomerate area, the area fraction for a certain size interval ($X_{[i,ii]}$) and the cumulative area frequency ($F_{[i,ii]}$) agglomerates, representing the total area fraction considering a certain area interval, that are given by:

$$X_{[i,ii]} = \frac{A_{[i,ii]}}{\sum_{i=1}^{n} A_{[i,ii]}} \times 100 \quad (2)$$

$$F_{[i,ii]} = \frac{\sum_{i=1}^{ii} A_{[i,ii]}}{\sum_{i=1}^{n} A_{[i,ii]}} \times 100 \quad (3)$$

where $A_{[i,ii]}$ represents one area interval.

Figure 2 and Table 1 show the final morphology, the values of the corresponding mixing indices and the electrical resistivity of the nanocomposites prepared with the various mixing routes.

The PP/CNF system is reasonably well dispersed by the twin screw extruder (Area ratio = 7,9%, with circa 30 % of the agglomerates having areas in the range 5 to 20 μm^2). Repetitive converging/ diverging flows ("RINGS") were more efficient in terms of dispersion (Area ratio = 1,2% and around 15 % of the agglomerates with areas between 5 to 20 μm^2). The "TWIN+RINGS" method lead to a small improvement on the dispersion level (Area ratio = 6,1%), compared to the extruded composite.

The results showed that functionalization improved the dispersion by twin screw extrusion, but the opposite effect was observed using the "RINGS" method.

Volume resistivity decreased with increasing dispersion level for the composites with pure and functionalized CNT.

Chemical functionalization improved the CNF /polymer interface, as illustrated in Figure 3 for composites prepared by twin screw extrusion.

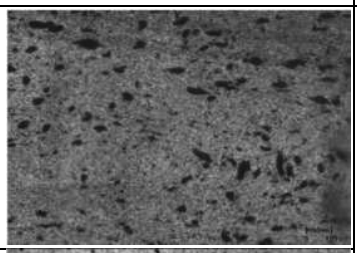
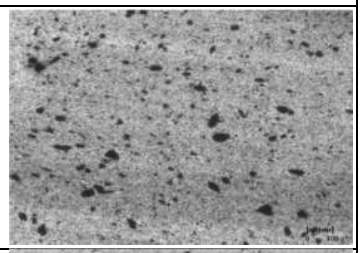
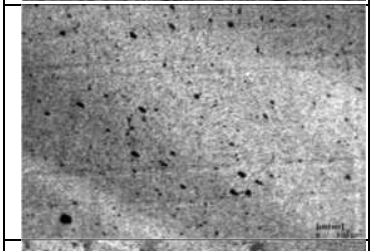
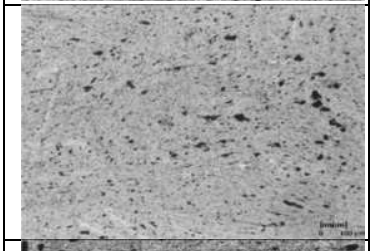
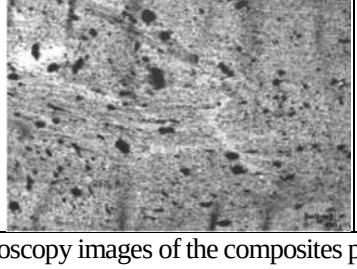
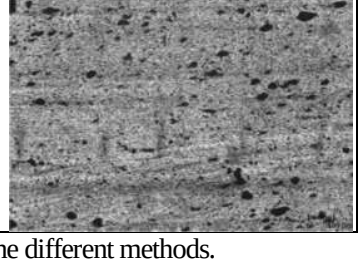
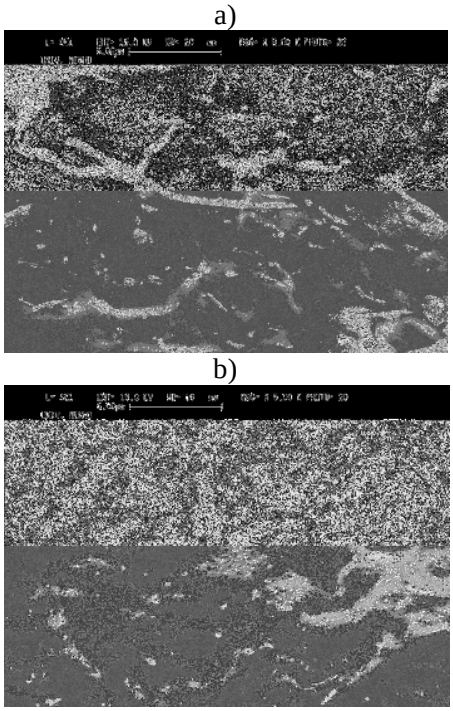
Melt mixing method	Sample	Typical OM image	Sample	
TWIN	PP + 5% CNF		PP + PP-g-MA + 5% FCNF (4.25% CNF)	
RINGS				
TWIN+RINGS				

Fig. 2. Optical microscopy images of the composites produced by the different methods.

Table 1. Dispersion indices and electrical resistivity of the composites produced by the different melt mixing routes.

Sample	Melt mixing method	Area ratio (%)	Average agglomerate area (μm^2)	Nº of agglomerates (per mm^2)	$X_{[5,20]}$ (%)	Agglomerates cumulative area frequency (%)			Volume resistivity/ (10^{10} Ω.m)
						$F_{[5,100]}$	$F_{[5,200]}$	$F_{[5,400]}$	
PP + 5% CNF	TWIN	7,9 ± 1,7	100 ± 17	810	30,5	72,2	86,6	96,1	2,5 ± 0,5
	RINGS	1,2 ± 0,2	70 ± 9	170	14,9	86,1	94,4	98,4	0,6 ± 0,5
	TWIN+ RINGS	6.1 ± 1	80 ± 30	810	37,9	78,3	90,9	98,6	0,7 ± 0,4
PP + P -g-MA + 5% FCNF (4.25% CNF)	TWIN	5.8 ± 1	90 ± 20	670	26,2	77,7	90,0	96,2	1,9 ± 0,5
	RINGS	2.6 ± 0,3	80 ± 10	301	29,5	83,5	92,8	97,3	0,2 ± 0,3
	TWIN+ RINGS	7.4 ± 1	60 ± 20	1430	53,4	89,3	95,7	98,6	2,3 ± 0,1

a)



b)

Fig. 3. SEM micrographs of the cross-sections of composites with a) pure and b) functionalized CNF.

Conclusions

Composites with CNF, pure and chemically functionalized, and PP, were prepared using two different melt mixing methods, separately and in sequence. The CNF distribution, dispersion and primary agglomerate size for the composites obtained by the different methods was analysed by optical microscopy. The effect of CNF functionalization on its dispersion, agglomerate size, and CNF/polymer interface was studied by optical microscopy and scanning electron microscopy.

The composites produced by the "RINGS" method presented a higher dispersion level as compared to the "TWIN" method, for the pure and functionalized CNF composites. The application of the "RINGS" method to the composite produced by twin screw extrusion had a residual effect on the CNF dispersion, slightly improving the dispersion of the pure CNF and increasing the total agglomerate area of the FCNF composites.

A correlation between volume resistivity and area ratio for all composites was observed, since increasing dispersion lead to lower resistivity composites.

Finally the CNF functionalization was shown to improve the nanofiber /polymer interface.

Acknowledgments

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